

Group A: Unit-1 Atomic structure:

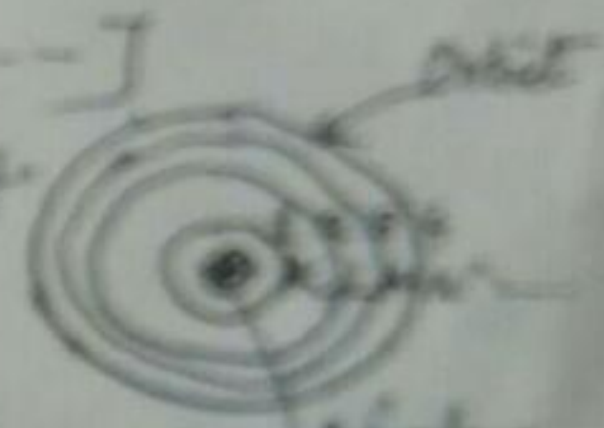
⇒ Defects of Rutherford's atomic theory/model:

- Rutherford's planet like model of atom, was contested by Niels Bohr on two grounds:
1. According to Classical theory, the negatively charged rotating electrons will continuously emit radiation and thus they will rotate on a spiral path. A time comes when it will ultimately collide with the nucleus and thus the atom will collapse. No such thing is however observed as atom is stable system.
 2. If the electrons lose energy continuously, the observed atomic spectrum should be continuous, consisting of broad bands emerging one into another. However, observed atomic spectrum consists of well defined lines of definite frequencies, i.e; discontinuous.

⇒ Bohr's atomic theory/model:

In order to overcome the defects of the Rutherford's atomic theory/model and also to explain the spectrum of H-atom, Niels Bohr (1913) proposed a quantum mechanical model of the atom on the basis of Planck's quantum theory. The main features of this model are:

1. Electrons revolve around the nucleus in certain definite circular paths, called orbits or shells. Orbits have fixed size or radius, given by $r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z} = n^2 r_0$ [where $r_0 = \text{Bohr radius} = 0.529 \text{ \AA}$, $Z = \text{atomic no. of atom/nuclear charge}$, $n = \text{Orbit number}$]
2. Each orbit is associated with definite energy, so called energy levels or energy shells. These orbits are designated as K, L, M, N, O, P, ...; energy order of these orbits is $K < L < M < N < O < \dots$. Energy of orbits given as $E_n = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^2} = -\frac{E_0 Z^2}{n^2}$ [where $E_0 = \text{Bohr's energy} = 21.79 \times 10^{-19} \text{ J/atom}$ or, 13.6 eV/atom or, 313.5 Kcal/atom , $Z = \text{at. no. of atom}$, $n = \text{no. of orbit} = 1, 2, 3, 4, \dots$]
3. As long as an electron is revolving in an orbit it neither loses nor gains energy. Hence, these orbits are also called stationary states. Orbit of lowest energy (i.e, K-shell) is called Ground state, and others (L, M, N, O, ...) are excited states.
4. When energy is supplied to an electron, it absorbs energy in fixed amounts (one quanta) and jumps to higher energy state (excited state). Since excited state is unstable, the electron may jump back to the lower energy state and in doing so, it emits the same amount of energy.



Energy change during electronic transition, $\Delta E = E_2 - E_1 = h\nu$ (one quanta).
 [where $E_1, E_2 = \text{energies of electron in two orbits}$, $\nu = \text{frequency of radiation absorbed or emitted}$, $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ Js}$].

- If $E_1 > E_2$, $\Delta E = -ve$, i.e; energy emitted. Here emission (bright) spectrum observed.
 If $E_1 < E_2$, $\Delta E = +ve$, i.e; energy absorbed. Here absorption (dark) spectrum observed.
5. Only those energy orbits are permitted for the electron in which the angular momentum is a whole number multiple of $\frac{h}{2\pi}$, i.e; $mvr = \frac{nh}{2\pi}$ [where $m = \text{mass of electron}$, $v = \text{velocity of electron}$, $r = \text{radius of orbit}$, $h = \text{Planck's constant}$, $n = \text{no. of orbit} = 1, 2, 3, \dots$].
 For 1st, 2nd, 3rd... orbits angular momentum = $\frac{h}{2\pi}$, $\frac{2h}{2\pi}$, $\frac{3h}{2\pi}$ respectively. Thus, angular momentum of the electron is quantised.

Merits/Advantages of Bohr's atomic model: (i) This explains stability of an atom.
 (ii) This helps in calculating the radius, energy of an orbit, velocity of an electron.
 (iii) This satisfactorily explains spectra of species having one electron, e.g. H, He⁺, Li²⁺ etc.

Defects or limitations of Bohr's atomic model:
 (i) It does not explain the spectra of species having more than one electron, e.g. He, Li⁺, Be²⁺ etc.
 (ii) Fine lines observed in the spectra of atoms/ions by high resolving spectroscopic, don't explain.
 (iii) No justification was given for the principle of quantisation of angular momentum, i.e; $mvr = \frac{nh}{2\pi}$, not $mvr = \frac{h}{3\pi}$ or $\frac{h}{4\pi}$.
 (iv) It does not explain splitting of spectral lines into groups of fine lines under influence of

magnetic field (Zeeman's effect) and electric field (Stark's effect)

*) This is against the Heisenberg's Uncertainty Principle. It is incompatible with wave nature of electrons.

→ Bohr-Sommerfeld's atomic theory/model:

To account for the fine structure in the spectrum of H-atom, Sommerfeld⁽¹⁹¹⁵⁾ extended or modified Bohr's theory, called Bohr-Sommerfeld's atomic theory. The main features/postulates of this theory are -

1. Each orbit except the 1st orbit (K-shell) is made of sub-orbits/sub-shells.

The number of sub-orbits in an orbit is equal to the orbit number.

2. The sub-orbit may be circular as well as elliptical. If there is more than one sub-orbits in an orbit then one sub-orbit will be circular and the rest will be elliptical.

3. The various sub-orbits of an orbit have very slightly different energies.

Thus, according to Sommerfeld the 3rd orbit (M-shell) will be made of one circular and two elliptical sub-orbits as shown in Fig-1.

Sommerfeld introduced the concept of Principal and azimuthal quantum nos., such that

$$\frac{\text{Principal Q.No. (n)}}{\text{Azimuthal Q.No. (l)}} = \frac{\text{Length of major axis of a sub-orbit}}{\text{Length of minor axis of the sub-orbit}}$$

For 3rd orbit, the value of principal Q.No. (n) is 3. Hence, the azimuthal Q.No. (l) will have values from 1 to 3, i.e., 1, 2, 3.

(i) When $n=3$ & $l=3$; sub-orbit is circular, whose major & minor axes are equal.

(ii) When $n=3$ & $l=2$; sub-orbit is elliptical, whose major axis is $3/2$ times longer than its minor axis.

(iii) When $n=3$ & $l=1$; sub-orbit is also elliptical, whose major axis is 3 times longer than its minor axis.

This model is capable of explaining splitting of the spectral lines of H-atom.

According to this theory, the energy of electron depends not only on the principal Q.No. (n) but also to some extent azimuthal Q.No. (l). The frequency of the radiation emitted as a result of transition of an electron from a energy level E_2 to an energy level E_1 ($E_2 > E_1$) would, therefore, vary depending on the various values of l. As a result, a group of closely spaced lines would appear instead of a single line in the spectrum of H-atom/H-like ions.

Limitations/Defects of Sommerfeld's theory/model:

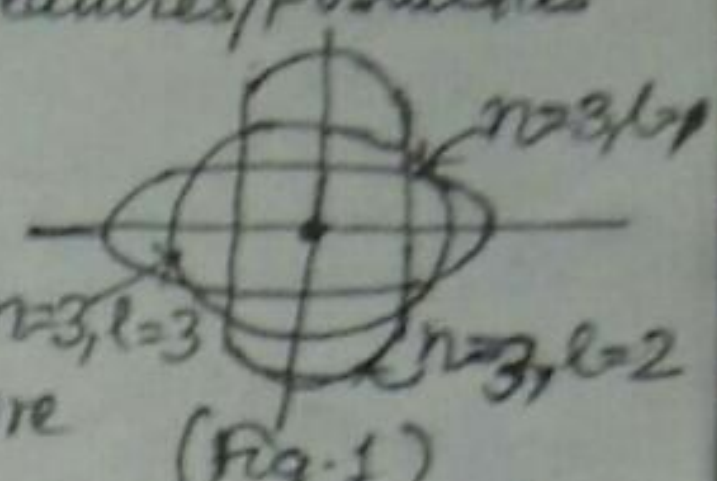
1. This theory/model could not explain with mathematical exactness, the spectra of atoms/ions containing more than one electron.

2. This cannot give the correct number of lines observed in fine structure.

3. The exact definition of position and momentum is contrary to the uncertainty principle.

⇒ Bohr's explanation of Hydrogen Spectrum:

Although H-atom contains only one electron, yet its spectrum comprises of a large number of lines. This is because any given sample of hydrogen contains almost infinite number of atoms. In normal condition, the electron of each H-atom remain in ground state (i.e., K-shell, $n=1$). When energy is supplied to sample of hydrogen gas by passing an electric discharge through H_2 gas, individual atoms absorb different amount of energies and shifted to higher levels 2nd, 3rd, 4th etc. The electrons in higher energy level are relatively unstable and hence drop back to



Lower energy levels emitting energy in the form of a photon of light of specific wavelength/frequency and thus gives different lines in the spectrum of H-atom.

Lines appearing in atomic spectrum due to drop of electrons from higher energy levels (2, 3, 4, 5, 6...) to the lowest energy level (i.e., 1st or K-shell) were discovered by Lyman and hence named as Lyman series. Lines appearing due to drop of electrons from energy levels (3, 4, 5, 6...) to the energy level 2 (i.e., L-shell) were named as Balmer series.

Similarly, the Paschen, Brackett and Pfund series correspond to drop of electrons from higher energy levels to energy levels 3, 4 & 5 respectively.

Maximum number of lines produced when an electron jumps from n^{th} level to ground level is equal to $\frac{n(n-1)}{2}$. For example, in case of $n=4$, number of lines produced is 6. Values of n_1, n_2 for various spectral lines of H-atom with the region in which they appear are given in Table-1.

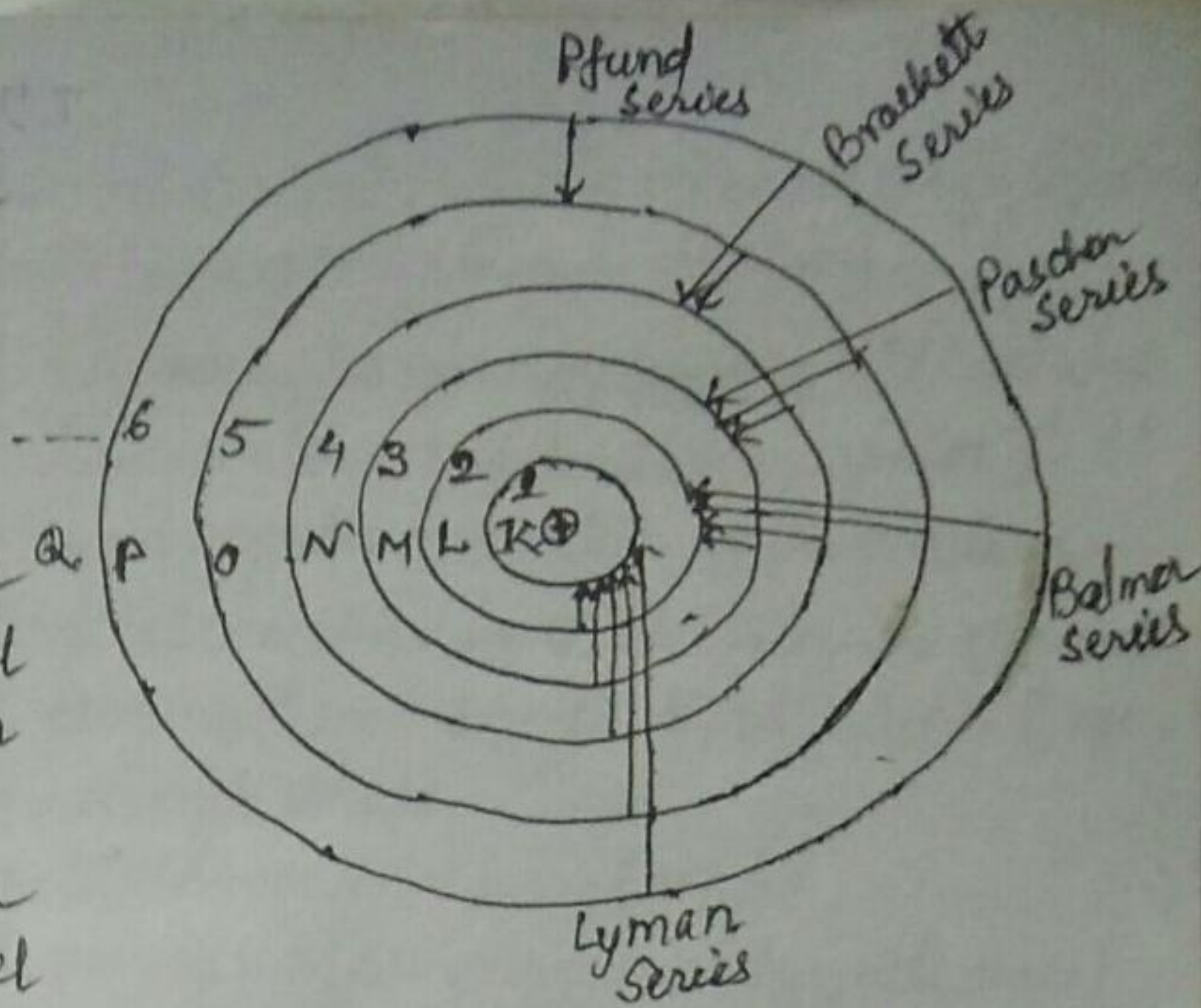


Table-1

Spectral line series	Electron jumps to an energy level with n_1	Electron jumps from energy level with n_2	Spectral region	Wavelength (λ) in \AA $[\frac{1}{\lambda} = R_H (\frac{1}{n_1^2} - \frac{1}{n_2^2})]$ where $R_H = \text{Rydberg's Const. } (1.097 \times 10^7 \text{ m}^{-1})$
1. Lyman Series	1	2, 3, 4, 5, 6...	Ultra Violet	Less than 4000\AA
2. Balmer series	2	3, 4, 5, 6...	Visible	$4000 - 7000 \text{\AA}$
3. Paschen Series	3	4, 5, 6, 7...	Near Infra-red	More than 7000\AA
4. Brackett Series	4	5, 6, 7...	Far infrared	$> 10,000 \text{\AA}$
5. Pfund Series	5	6, 7, ...	"	"

Quantum Numbers:

Just like postal address of a person, four identification numbers are required to specify energy, shape, orientation and spin of a particular electron in an atom, called quantum numbers. First three numbers have been deduced from Schrodinger wave equation while fourth relates spinning motion of electron. Thus, "quantum numbers are the set of four numbers which give a complete information about the electron in an atom, i.e. its energy, shape, orientation and spin".

- Quantum numbers are:
1. Principal quantum number (n)
 2. Azimuthal or angular or subsidiary quantum no. (l)
 3. Magnetic quantum number (m)
 4. Spin quantum number (s)

1. Principal quantum number: This quantum no. was given by Bohr. It describes average distance of electron from nucleus and also energy associated with it, i.e. energy level or shell. It is denoted by symbol ' n ', and has integral values from 1 to ∞ .

Value of n :	1	2	3	4	5	6	7...
Orbit/shell:	K	L	M	N	O	P	Q

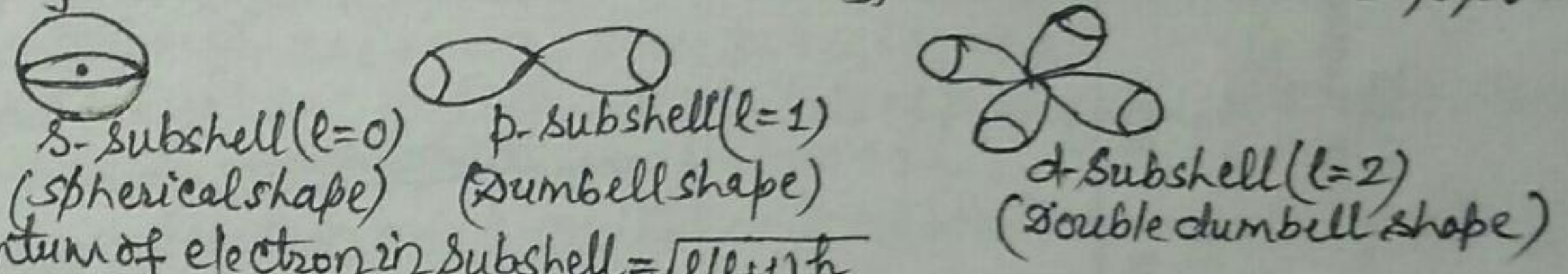
Angular momentum of electron in an orbit,
 $mvr = \frac{nh}{2\pi}$ (where $n = \text{principal \& no.}$)

- (i) Higher the value of n (i) greater is the distance of electron orbit from the nucleus ($r \propto n^2$).
- (ii) Greater is the magnitude of energy of orbit/electron ($E_n \propto \frac{1}{n^2}$).

The maximum number of electrons present in an orbit = $2n^2$ (Where n = Principal Q. No ~ Orbit no)
No energy orbit in the atoms of known elements possess more than 32 electrons

2. Azimuthal Quantum number: This quantum number was given by Sommerfeld and also called secondary, subsidiary or angular quantum number. It is denoted by symbol ' l '. It describes spatial distribution of electron cloud & angular momentum of the electron. Actually, it indicates the shape of suborbit/orbital occupied by the electron. The value of l depends upon the value of n , and values of l ranging from 0 to $(n-1)$. Each value of l represents one particular subshell/suborbit and definite shape.

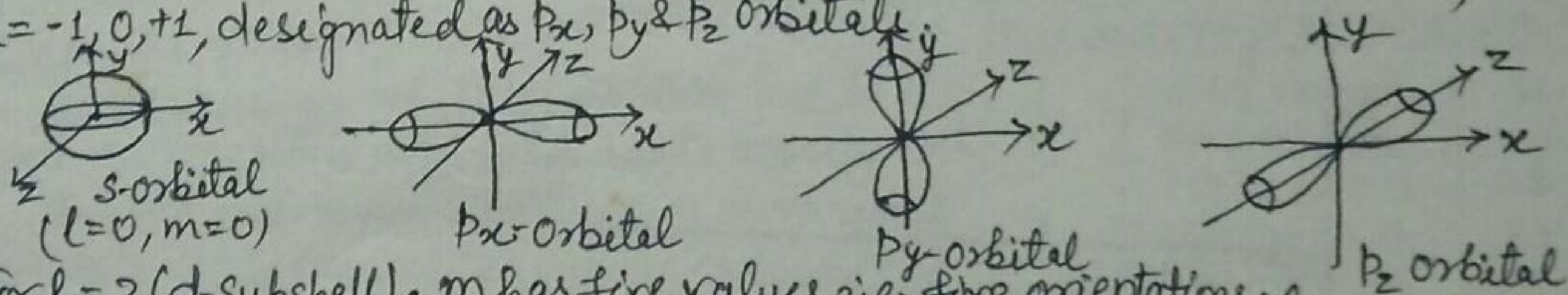
Thus, $n=1$ (K-shell) has $l=0$, ^{2.e.} One subshell (s) having spherical shape.
 $n=2$ (L-shell) has ^{two} l values: 0 & 1, ^{2.e.} two subshells: s (spherical), p (dumbbell shape).
 $n=3$ (M-shell) has three l values; 0, 1 & 2, ^{2.e.} three subshells: s (spherical), p (dumbbell) & d (double dumbbell shape).
 $n=4$ (N-shell) has four l values; 0, 1, 2 & 3, ^{2.e.} four subshells, s, p, d & f (undefined shape).
Designation of subshells - s, p, d & f are derived from certain spectroscopic terms ^{characters} sharp, principal, diffuse & fundamental. The order of energies of various subshells in the same shell (n) is $s < p < d < f$. Subshells having equal l values but with different n -values have similar shapes but their sizes increase as the value of n increases. Maximum number of electrons can accommodate in different subshells are 2, 6, 10 & 14 respectively.



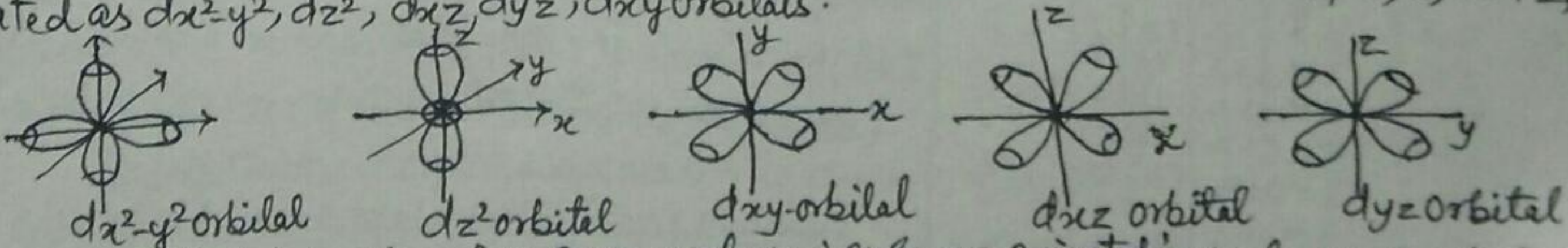
Angular momentum of electron in subshell = $\sqrt{l(l+1)} \frac{h}{2\pi}$

e.g. for p-orbital or subshell, $l=1$; Angular momentum = $\sqrt{1(1+1)} \frac{h}{2\pi} = \frac{\sqrt{2}h}{2\pi} = \frac{h}{\sqrt{2}\pi}$

3. Magnetic quantum number: This quantum number was given by Linde to explain Zeeman's effect (splitting of single spectral line into a number of closely spaced lines in the presence of magnetic field, due to electron present in a particular subshell acquire certain specific orientations in space called orbitals) It describes the orientation of electron cloud (orbital). It is denoted by symbol m . m has $(2l+1)$ values ranging from $-l$ to $+l$ including 0. For $l=0$ (s-subshell), m has only one value, $m=0$ (s-orbital, which is non-directional). For $l=1$ (p-subshell), m has three values, i.e. three orientations, $l = -1, 0, +1$, designated as p_x, p_y & p_z orbitals.



For $l=2$ (d-subshell), m has five values, i.e. five orientations; $l = -2, -1, 0, +1, +2$, designated as $d_{x^2-y^2}, d_{z^2}, d_{xz}, d_{yz}, d_{xy}$ orbitals.



For $l=3$ (f-subshell), m has seven values, i.e. seven orientations; $l = -3, -2, -1, 0, +1, +2, +3$, designated as $f_x(x^2-y^2), f_y(x^2-y^2), f_z(x^2-y^2), f_{xyz}, f_{yz^2}, f_{xz^2}, f_{z^3}$. Their shapes are complicated. Orbitals of same subshell are equivalent in energies (degenerate) and electron density. Each orbital can occupy/accommodate two electrons of opposite spins (11).

No. of orbitals in a subshell = $(2l+1)$; No. of orbitals in a shell = n^2
Angular momentum of electron in an orbital = $\sqrt{l(l+1)} \cos \theta$ (where θ = Orientation)

4. Spin quantum numbers: This quantum no. was given by Goudsmit and designated as s . An electron besides charge & mass also spins around its axis and this leads to quantum number called spin quantum number, i.e. this quantum no. describes spin of electron in an orbital. Since an electron can spin either in clockwise or anticlockwise direction, s can have two values $+\frac{1}{2}$ & $-\frac{1}{2}$. $s = +\frac{1}{2}$ shown by \uparrow or \curvearrowright (clockwise spin); $s = -\frac{1}{2}$ shown by \downarrow or \curvearrowleft (anticlockwise spin).

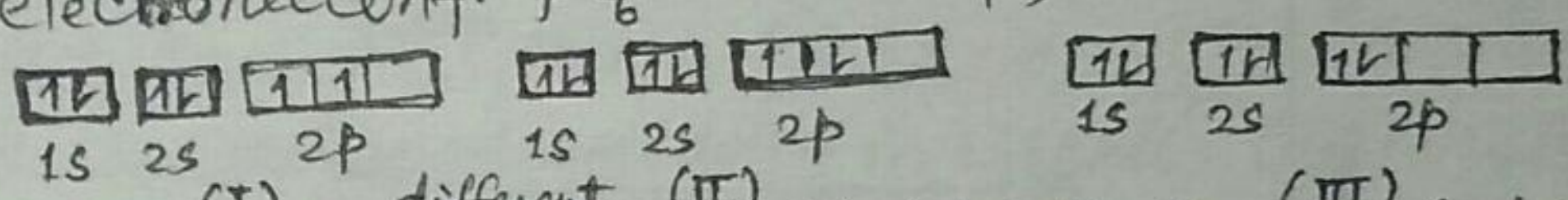
This quantum no. leads to spin angular momentum, $m_s = \sqrt{s(s+1)} \frac{h}{2\pi} = \sqrt{3/2} \frac{h}{2\pi}$ ($\because s = \pm 1/2$)

→ Rules governing electronic configuration:

1. Hund's rule or Hund's rule of maximum spin multiplicity: Hund has given a new rule to write down orbital electronic conf. (Orbital or box diagram) which associated with maximum spin multiplicity of electron in any orbital, known as Hund's rule.

It is stated as "Electrons have the tendency to remain unpaired in an incompletely filled orbital/subshell so as to have maximum spin multiplicity, minimum energy and maximum stability." In other words, "Orbitals of same energy (degenerate) are filled up first singly with parallel spins and then paired up with opposite spins."

For example, electronic conf. of C_6 is $1s^2 2s^2 2p^2$, but its three orbital/box diagrams can be expected:



Case-I Electrons are present in two different p-orbitals of p-subshell with same spins (clockwise), Spin multiplicity $(2s+1) = 2 \times 1 + 1 = 3$; Since $S = +\frac{1}{2} + \frac{1}{2} = 1$

Case-II Electrons are present in two different orbitals of p-subshell with opposite spins. So, $S = +\frac{1}{2} - \frac{1}{2} = 0$; Spin multiplicity $(2s+1) = 2 \times 0 + 1 = 1$.

Case-III Electrons are present in one p-orbital with opposite spins. So, $S = +\frac{1}{2} - \frac{1}{2} = 0$; Spin multiplicity $(2s+1) = 2 \times 0 + 1 = 1$.

Thus, out of these three ele. confs, (I) will be most stable, and so correct by this rule.

* By this rule, order of stability of ele. conf. Completely filled > Half filled > Incompletely filled.

2. Aufbau principle: This principle was given by Pauli. 'Aufbau' (actually of 'bau') is a German word, meaning 'building up'. Thus, the process of filling up of electrons in the different subshells/orbitals on the basis of increasing order of their energies is called Aufbau principle. According to this principle, (i) The electron enters to that subshell/orbital first for which the value of $(n+l)$ is minimum, i.e., Orbital $(n+l)$. (ii) If the $(n+l)$ value is same for two orbitals, the electron enters to the orbital for which the value of n is minimum (least).

Lower energy orbitals are, therefore, better seats for electrons and better seats occupy first.

The increasing order of energies of various orbitals is: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$. (By table) It is noted $nd < (n-1)d$; $(n-1)p < ns < (n-1)d$, but $6s < 4f < 5d/7s < 5f < 6d$ (Lanthanides/Actinides)

Using this principle, we can write down electronic conf. of elements/ions easily.

But there are some exceptional cases given below:

(i) In Cr, Mo (Gr. 6) ele. conf. disobey this principle.

e.g. Cr_{24} : $3d^4 4s^2$ (By Aufbau principle) → $3d^5 4s^1$ (Correct) (unstable) (Incorrect) (stable)

Mo_{42} : $4d^4 5s^2$ → $4d^5 5s^1$ Hence, d4 conf. should be changed to d5 (half filled) in ground state conf.

n value	l value	(n+l) value	Orbital	Pref. Order
1	0(s)	1+0=1	1s	1
2	0(s)	2+0=2	2s	2
	1(p)	2+1=3	2p	3
3	0(s)	3+0=3	3s	4
	1(p)	3+1=4	3p	5
	2(d)	3+2=5	3d	7
4	0(s)	4+0=4	4s	6
	1(p)	4+1=5	4p	8
	2(d)	4+2=6	4d	10
	3(f)	4+3=7	4f	14
5	0(s)	5+0=5	5s	9
	1(p)	5+1=6	5p	12
	2(d)	5+2=7	5d	15
	3(f)	5+3=8	5f	18
6	0(s)	6+0=6	6s	13
	1(p)	6+1=7	6p	16
	2(d)	6+2=8	6d	19
	3(f)	6+3=9	6f	22
7	0(s)	7+0=7	7s	21
	1(p)	7+1=8	7p	24
	2(d)	7+2=9	7d	27
	3(f)	7+3=10	7f	30

In Cu, Ag, Au (Gr. 11) ele. Conf. disobey this rule
 $Cu_{29}: 3d^9 4s^2$ (By Aufbau principle) \rightarrow $3d^{10} 4s^1$ (Symmetrical & more exchange energy)
 unstable (incorrect) Stable (correct)

Hence, d^9 Conf. should be changed to d^{10} (Completely filled)
 In f-block elements, $(n-2)f$ orbital occupy only when $(n-1)d$ orbital occupy at least one electron. In f-block elements, $(n-2)f^6 (n-1)d^1$ Conf. should be changed to $(n-2)f^7 (n-1)d^0$ Conf. and $(n-2)f^{13} (n-1)d^1$ should be changed to $(n-2)f^{14} (n-1)d^0$ (stable).

Pauli exclusion principle: Pauli (1925) has given a very important principle which determines the maximum number electrons in the orbits/sub orbits/orbitals, known as Pauli exclusion principle. According to it "No two electrons of an atom has all the four quantum numbers same." Thus, two electrons present in an atom can have maximum of three quantum numbers same, i.e. they can be present in the same orbit, suborbit & orbital. However, they must have opposite spins, i.e. different spin quantum numbers.

For example, two electrons present in K-shell possess the following values of Q.Nos: $n=1, l=0, m=0$ & $s=+\frac{1}{2}$ or $-\frac{1}{2}$, i.e. there are two sets of Q.Nos. $\{1, 0, 0, +\frac{1}{2}\}$ & $\{1, 0, 0, -\frac{1}{2}\}$. Hence, K-shell can accommodate maximum of two electrons of opposite spins. $\frac{1\uparrow}{1s}$

Similarly for 2nd shell (L-shell), there are eight sets of four quantum nos. $\{2, 0, 0, +\frac{1}{2}\}, \{2, 0, 0, -\frac{1}{2}\}, \{2, 1, -1, +\frac{1}{2}\}, \{2, 1, -1, -\frac{1}{2}\}, \{2, 1, 0, +\frac{1}{2}\}, \{2, 1, 0, -\frac{1}{2}\}, \{2, 1, 1, +\frac{1}{2}\}, \{2, 1, 1, -\frac{1}{2}\}$. Hence, eight electrons can be accommodated in L-shell. $\frac{1\uparrow}{2s} \frac{1\uparrow}{2p} \frac{1\uparrow}{2p} \frac{1\uparrow}{2p}$

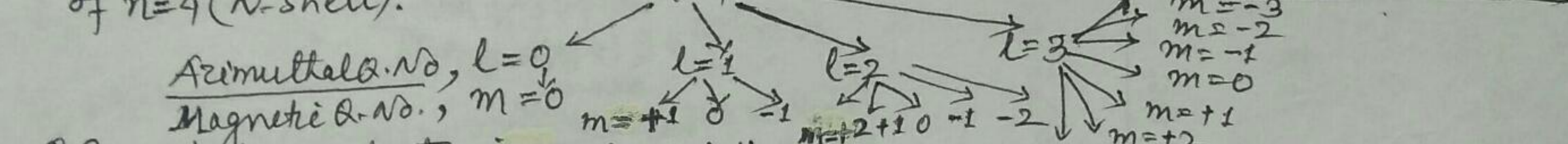
Since more than the prescribed number of electrons are excluded (not accommodated) from an orbit/suborbit according to Pauli, hence this is called Pauli's exclusion principle.

Text questions

Q.1. Write down all the four quantum nos. of 28th electron in Ni_{28} atom.

Ans. Ele. Conf. of Ni_{28} is $[Ar_{18}] 3d^8 4s^2$, 28th electron of Ni-atom present in 3d-subshell.

Box representation of 3d-electrons: $\frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d}$ Principal Q.No (n) = 3, Azimuthal Q.No (l) = 2, Mag. Q.No (m) = 0, Spin Q.No (s) = $-\frac{1}{2}$ (anticlockwise)



Q.3. Write down electronic conf. of following:

$Cr_{24}, Cu_{29}, Br_{35}, Sn_{50}, Ce_{58}, Hg_{80}, Fe_{26}^{3+}, Mn_{25}^{2+}, Co_{27}^{3+}, I_{53}^{2-}, Ag_{47}^+$
 Ans. $Cr_{24}: [Ar_{18}] 3d^5 4s^1$; $Cu_{29}: [Ar_{18}] 3d^{10} 4s^1$; $Br_{35}: [Ar_{18}] 3d^{10} 4s^2 4p^5$
 $Sn_{50}: [Kr_{36}] 5s^2 5p^2$; $Ce_{58}: [Xe_{54}] 4f^1 5d^1 6s^2$; $Hg_{80}: [Xe_{54}] 5d^{10} 6s^2$
 $Fe_{26}: [Ar_{18}] 3d^6 4s^2$; $Fe^{3+}(23e): [Ar_{18}] 3d^5$; $Mn_{25}: [Ar_{18}] 3d^5 4s^2$, $Mn^{2+}(23e): [Ar_{18}] 3d^5$
 $Co_{27}: [Ar_{18}] 3d^7 4s^2$, $Co^{3+}(24e): [Ar_{18}] 3d^6$; $I_{53}^{2-}(54e): [Xe_{54}]$ or $[Kr_{36}] 4d^{10} 5s^2 5p^6$
 $S_{16}^{2-}(18e): [Ar_{18}]$ or $[Ne_{10}] 3s^2 3p^6$. $Ag_{47}^+(46e): [Kr_{36}] 4d^{10}$

Q.4. Explain why Chromium (Cr_{24}) shows $[Ar_{18}] 3d^5 4s^1$, not $[Ar_{18}] 3d^4 4s^2$ Conf?

Ans. $Cr_{24}: [Ar_{18}] 3d^5 4s^1$ or $[Ar_{18}] \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{3d} \frac{1\uparrow}{4s}$, not $[Ar_{18}] 3d^4 4s^2$ Conf?
 Due to symmetrical and more exchange energy of above ele. Conf., it is more stable than that of $3d^4 4s^2$ Conf; which is less stable as it is unsymmetrical. Hence, Chromium shows $[Ar_{18}] 3d^5 4s^1$ Conf, not $[Ar_{18}] 3d^4 4s^2$.